Plasma enhanced chemical vapor deposition of thermally stable and low-dielectric-constant fluorinated amorphous carbon films using low-global-warming-potential gas C_5F_8

Tatsuru Shirafuji[a,*], Akira Kamisawa[b], Takaaki Shimasaki[b], Yasuaki Hayashi[a], Shigehiro Nishino[a]

[a]*Department of Electronics and Information Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*
[b]*Semiconductor Process Research and Development Division, ROHM Co., Ltd., 21, Saiin Mizosaki-cho, Ukyo-ku, Kyoto 615-8585, Japan*

Abstract

Low-dielectric-constant fluorinated amorphous carbon films have been prepared from the low global-warming-potential gas of C_5F_8 by a capacitively coupled plasma enhanced chemical vapor deposition method. Films were prepared at substrate temperatures as high as 400°C. The obtained deposition rate of 15–65 nm/min was higher than that of conventional C_4F_8 plasma at the same substrate temperature. The dielectric constant of the films varied from 2.1 to 2.5 with increasing RF power from 10 to 100 W. The residual thickness of the films after 400°C-thermal treatment was higher than 98%. At an RF power higher than 50 W, cracks appeared in the films that were rapidly cooled from 400°C to room temperature, and poor adhesion characteristics were obtained even for the samples without cracks after gradual cooling. On the other hand, the samples prepared at 10 W showed no cracks and good adhesion on a crystalline silicon substrate regardless of the cooling rate. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: C_5F_8; Global warming potential; Plasma; Chemical vapor deposition; Low dielectric constant; Inter-metal dielectric

1. Introduction

Shrinkage of the metal-line spacing in ultra large scale integrated circuits requires inter-metal dielectric (IMD) with a low dielectric constant for reducing resistivity–capacitance time delay. For feature dimensions less than 0.18 μm, IMDs need to have a dielectric constant below 2.5 [1,2]. Amorphous fluorinated carbon (a-C:F) films and organic polymers are promising candidates for IMDs. There are many types of potential organic polymers with low dielectric constant (low-k), and much research has focused on spin-on materials

[2]. However, the increase in wafer size will require higher coating uniformity to achieve reproducibility, a minimized wafer handling sequence, and a smaller amount of solvent for reducing wastes. Vapor phase deposition techniques can meet these requirements. Plasma enhanced chemical vapor deposition (PE-CVD) is one of the techniques that can prepare IMD films from the vapor phase. Furthermore, with PE-CVD a cross-linked structure can be achieved in the films, in contrast with the vapor phase transport technique [3,4]. PE-CVD of a-C:F films as IMD material has already been reported by several researchers [4–8].

However, the most commonly used source gas for this technique is C_4F_8, which has a high global warming potential (GWP) of 8700 and atmospheric lifetime of 3200 years [9]. Therefore, substitutional gases with a

---

* Corresponding author.
E-mail address: sirafuji@dj.kit.ac.jp (T. Shirafuji).

lower GWP and lifetime are required from the viewpoint of environmental protection. Recently, C_5F_8, which has a GWP and lifetime as low as 100 and 1 year, has been introduced to the reactive etching processes [9]. In our previous report, we applied C_5F_8 gas to PE-CVD of low-k a-C:F films [10]. The films prepared at 100°C showed low-k of approximately 2.0 and had thermal stability up to 300°C, but not up to 400°C. In this paper, we report on the preparation of a-C:F films from C_5F_8 plasma with a high substrate temperature of 400°C for obtaining films that have thermal stability up to 400°C.

2. Experimental

Fig. 1 shows the schematic representation of the experimental setup. Films were deposited on (100) p^+-type (0.01–0.02 Ω cm) silicon substrates using a capacitively coupled RF (13.56 MHz) PE-CVD reactor. The diameter of the RF electrode and the distance between the electrode and grounded substrate holder were 150 and 30 mm, respectively. The substrate was a 6-inch silicon wafer, which was used because it is suitable for future investigations of the compatibility of the films with chemical mechanical polishing. The diameter of the substrate holder was 70 mm, which is less than the substrate diameter due to limitations of the present experimental setup. Therefore, only the center region of the substrate was heated, and all of the film characterizations were performed on a piece (10 × 10 mm) of the wafer quarried out of the 6-inch wafer.

The flow rate of C_5F_8 (Nippon Zeon Co., Ltd, ZFL-58) was 16 sccm, and the substrate temperature was 400°C. RF power was varied in the range of 10–100 W. The deposition conditions are listed in Table 1.
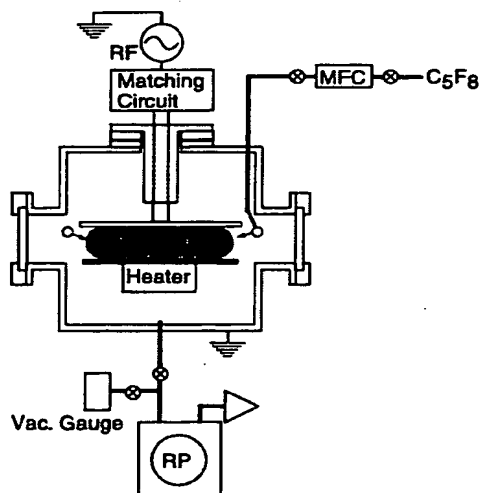

Fig. 1. Schematic representation of film deposition system.

Table 1
Typical deposition condition

Substrate temperature	400°C
RF power	10–100 W
Pressure	0.35 torr
C_5F_8 flow rate	16 sccm

The refractive index and thickness of the films deposited on the silicon substrates were determined by reflectance spectroscopy (Shimadzu UV-2500PC) with an incident angle of 5°. The measurements were performed in the wavelength range of 200–800 nm. Thickness was calculated from the period of interference pattern appearing in the reflectance spectra. The refractive index of the films was determined according to the observation that the reflectance at interference minima in the spectra were affected only by the value of the refractive index if the films were transparent. Refractive index was determined in the wavelength range of 600–800 nm. We performed characterization of the films, which had similar thicknesses of approximately 2.5–3 μm.

The structure of the films was investigated by X-ray photoelectron spectroscopy (XPS, JEOL JPS-9000SX). The take-off angle of the XPS measurements is 90°. The peak shift due to charging effects was calibrated by setting the C–F_2 peak position to 292.2 eV [11].

The thermal stability of the films was investigated by measuring residual thickness after thermal treatment at 400°C for 1 h in nitrogen ambient. Two types of cooling procedures were examined after thermal treatment. One was the gradual cooling, which took 1 h from 400°C down to 100°C. After that, samples were exposed to air and placed on a stainless steel brick at room temperature. The other procedure was rapid cooling, in which samples were exposed to air without a cooling period and then placed on a stainless steel brick.

The dielectric constant of the films was determined by measuring the capacitance of a metal–insulator–semiconductor (MIS) structure consisting of aluminum, film and p^+-type silicon at a frequency of 1 MHz.

Adhesion of the films was examined by a simple adhesive tape peel test using Scotch (3M) tape.

3. Results and discussion

3.1. Deposition rate

Fig. 2 shows the deposition rate of the films as a function of RF power. With increasing RF power from 10 to 50 W, the deposition rate increases from 15 to 65 nm/min. The deposition rate does not increase with
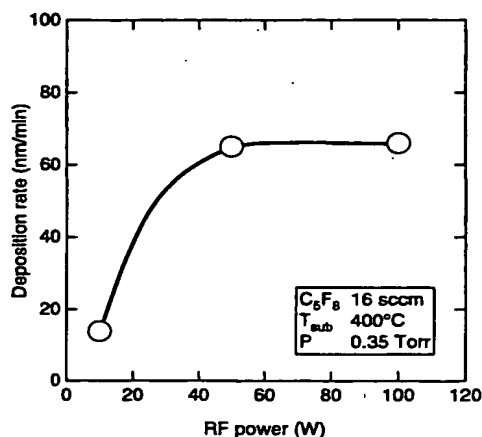
Fig. 2. Deposition rate of the films as a function of RF power.

Fig. 3. Dielectric constant of the films as a function of RF power.

RF power higher than 50 W. This is because the rate determining step is no longer the electron impact dissociation rate of source molecules but the source gas flow rate.

In our previous report using C_4F_8 under the same conditions where RF power was 40 W, no deposition was observed at 400°C [10] and a low deposition rate was also reported in other works [12] in which C_2H_2 or H_2 were mixed to enhance deposition rate. However, the mixing of hydrogenated monomers increased the dielectric constant to 2.4.

Therefore, the capability of C_5F_8 plasma to deposit films at the high substrate temperature of 400°C is another advantage over C_4F_8 in addition to its low GWP. Because the films deposited at 400°C are assumed to have thermal stability up to 400°C, we can expect preparation of low-k films with high thermal resistance.

3.2. Dielectric constant

Fig. 3 shows the dielectric constant of the films as a function of RF power. With increasing RF power, the dielectric constant increases from 2.1 to 2.5. This increase in the dielectric constant might be due to the dense films being prepared at high RF power, because the ratio of fluorine and carbon (F/C ratio) in the films and film structure investigated by XPS do not show marked differences except for the C–F_n bonding configuration described below. The dielectric constant of the films was also measured after thermal treatment, and there was no marked difference from the value before thermal treatment, which indicates that the films have thermal stability up to 400°C.

3.3. Thermal stability

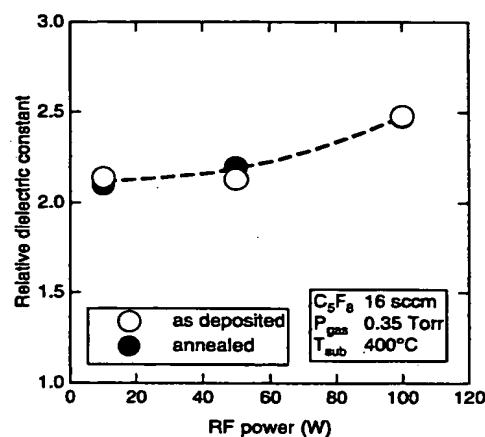Fig. 4 shows the thermal stability of the films as a

function of RF power. The residual thickness in the figure is the ratio of the thickness before and after thermal treatment. Since the preparation temperature is 400°C, most of the films keep their initial thickness after thermal treatment at 400°C. Only the films prepared at an RF power of 10 W show slight decreases in thickness, of which the cause is not clarified at present.

Fig. 5 shows the C(1s) region of the XPS spectra of the films before and after thermal treatment. Each spectrum has been deconvoluted to four peaks for C–CF, C–F, C–F_2 and C–F_3 bonds. All of the traces in Fig. 5 possess a common feature: the peak intensity for cross-linked C–CF bonds is higher than that for the other bonds. This feature was also observed in films deposited at the lower substrate temperature of 100°C as reported elsewhere [10]. As the film structure is not depending on substrate temperature, which can modify surface reactions, the deposition precursors from C_5F_8 plasma have the peculiar nature to form cross-linked structures.
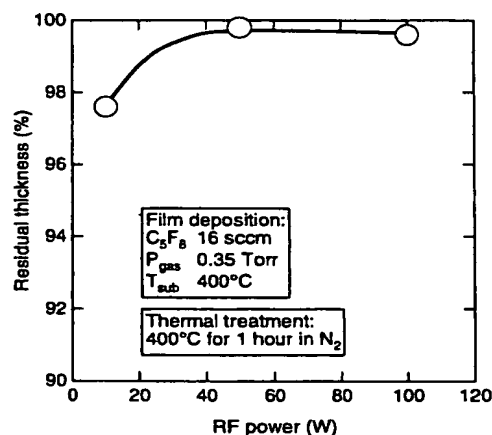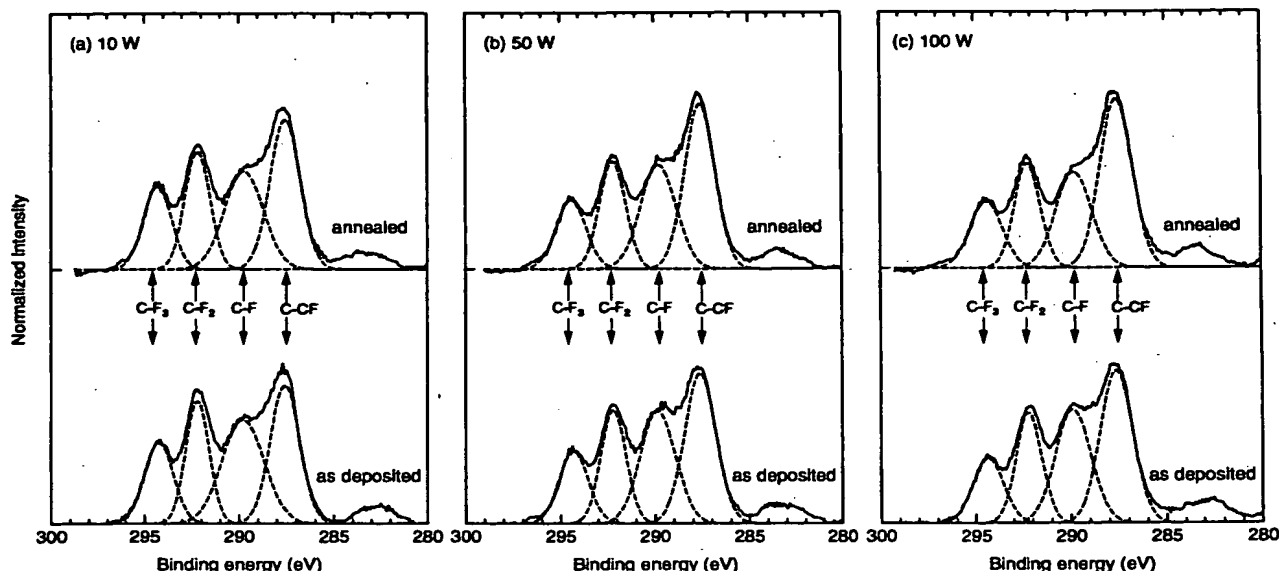

Fig. 4. Residual thickness as a function of RF power.

Fig. 5. C(1s) region of XPS spectra of films deposited at (a) 10 W, (b) 50 W and (c) 100 W. The bottom traces are as-deposited, and top ones are after thermal treatment at 400°C for 1 h in nitrogen ambient. Each spectrum is normalized by total integrated intensity.

Normalized integrated peak intensity for each bond was calculated from the spectra in Fig. 5 in order to quantify the change in $C-F_n$ composition in the films due to RF power difference and thermal treatment (Fig. 6).

As seen in Fig. 6a, the composition of cross-linked C–CF bonds increases with increasing RF power as expected from the characterization of dielectric constants. The peak intensity for C–F and $C-F_3$ bonds decreases with increasing RF power as seen in Fig. 6b,d, while that for $C-F_2$ bonds does not depend on RF power from the data for as-deposited films in Fig. 6c. These results indicate that cross-linked C–CF bonds

are preferentially created instead of C–F and $C-F_3$ bonds by increasing RF power.

The intensity of C–CF bonds increases further by thermal treatment as seen in Fig. 6a, which means that the cross-linking has progressed due to thermal treatment. On the other hand, the intensity for C–F bonds decreases by thermal treatment as shown in Fig. 6b. The peak intensity for $C-F_2$ and $C-F_3$ does not change as much as that for the C–CF and C–F bonds. These results indicate that C–F bonds are preferentially converted to cross-linked C–CF bonds with thermal treatment. In contrast to this structural change, however, the dielectric constant of the films does not change
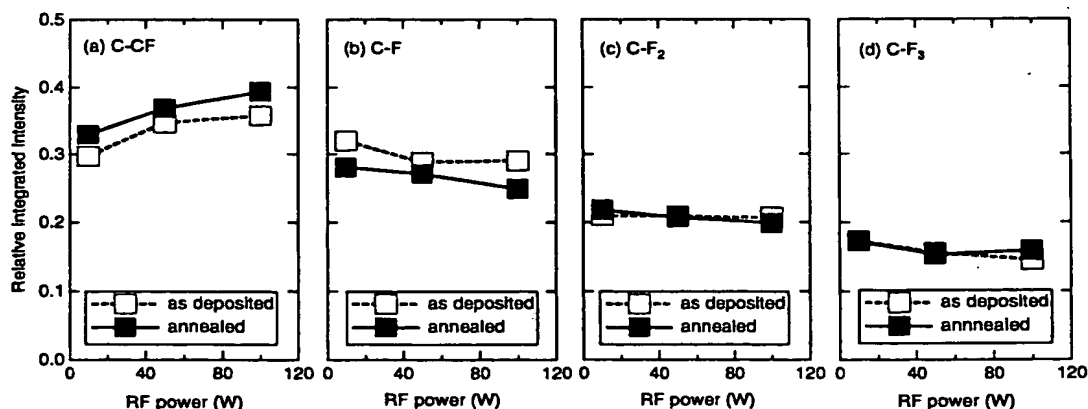

Fig. 6. Relative integrated peak intensity of (a) C–CF, (b) C–F, (c) $C-F_2$ and (d) $C-F_3$ bonds in the films before and after thermal treatment at 400°C for 1 h in nitrogen ambient.
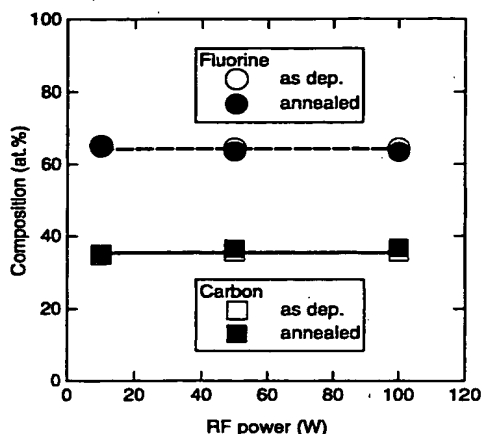
Fig. 7. Composition of the films before and after thermal treatment calculated from integrated peak intensity of C(1s) and F(1s) regions in XPS spectra.

Fig. 8. Cracks observed after rapid cooling from 400°C down to 100°C for 1–2 s.

after thermal treatment as shown in Fig. 3. While the spectrum of XPS reflects only the structure of the top surface of the films, the value of the dielectric constant reflects the entire bulk structure. Therefore, the increase in C–CF intensity and decrease in C–F intensity after thermal treatment are regarded as results of change in surface bonding configuration.

Fig. 7 shows the composition of carbon and fluorine in the films, before and after thermal treatment, as a function of RF power. The F/C ratio in the films is 2/1 and does not depend on RF power nor change even after thermal treatment. Although thermal treatment of the films might be accompanied with fluorine desorption out of the films as suggested by the fact that C–F bonds are converted to C–CF bonds, this result means that the amount of fluorine desorption is less than the resolution of the measurement for the F/C ratio.

3.4. Cracking and adhesion

Although the films showed thermally stable low-k characteristics, the films prepared at higher RF power showed several unfavorable characteristics. The samples at 400°C after deposition or thermal treatment were usually cooled gradually. However, when we cooled them rapidly, cracks were observed for the films prepared at a RF power higher than 50 W as shown in Fig. 8. This is due to the difference in thermal expansion coefficient between crystalline silicon and the films. Since the films prepared at higher RF power showed a higher dielectric constant and a more cross-linked structure, they might have a denser structure.

This tendency is also observed in the adhesive characteristics of the films. The films prepared at an RF power of 50 W or higher did not pass the tape-peel test

as shown in Table 2. Although cracks in the films were observed only for the samples cooled rapidly, the poor adhesion characteristics were observed even for the samples that were cooled gradually after film deposition and thermal treatment.

On the other hand, the films prepared at 10 W showed excellent adhesion properties and no cracks after gradual or rapid cooling after film deposition and thermal treatment. From the viewpoint of practical applications of low-k films, the low deposition rate of 15 nm/min for 10 W deposition is not favorable, and this must be improved in the future.

4. Conclusions

Fluorinated amorphous carbon films with low dielectric constant have been prepared from the low GWP gas C_5F_8 by a PE-CVD method. Films were prepared at substrate temperatures as high as 400°C.

Films deposited at a RF power of 50 W or higher showed a high deposition rate of 65 nm/min, dielectric constant of 2.2–2.5, and residual thickness of 99% or higher after thermal treatment at 400°C for 1 h in nitrogen ambient. However, these films showed poor adhesion characteristics on a crystalline silicon substrate. In addition, cracks in the films were observed if the films were cooled rapidly from 400°C.

The films deposited at a low RF power of 10 W showed a low deposition rate of 15 nm/min. However, dielectric constant was 2.1 and residual thickness was 98%. In addition, the 10-W films showed good adhesion on a crystalline silicon substrate and no cracks were observed even after rapid cooling.

Table 2
Results of tape-peel test

RF power	As-deposited	Annealed
10 W	PASS	PASS
50 W	FAIL	FAIL
100 W	FAIL	FAIL

References

[1]   W.W. Lee, P.S. Ho, MRS Bull. 22 (10) (1997) 19.
[2]   N.H. Hendricks, Mater. Res. Soc. Symp. Proc. 443 (1997) 3.
[3]   C.-I. Lang, G.-R. Yang, J.A. Moore, T.-M. Lu, Mater. Res. Soc. Symp. Proc. 381 (1995) 45.
[4]   K. Endo, T. Tatsumi, J. Appl. Phys. 78 (1995) 1370.
[5]   T.W. Mountsier, D. Kumar, Mater. Res. Soc. Symp. Proc. 443 (1997) 41.
[6]   C.B. Labelle, S.J. Limb, K.K. Gleason, J.A. Burns, Mater. Res. Soc. Symp. Proc. 443 (1997) 189.
[7]   T. Shirafuji, Y. Miyazaki, Y. Hayashi, S. Nishino, Plasmas Polym. 4 (1999) 57.
[8]   T. Shirafuji, Y. Miyazaki, Y. Nakagami, Y. Hayashi, S. Nishino, Jpn. J. Appl. Phys. 38 (1999) 4520.
[9]   Y. Ito, A. Koshiishi, R. Shimizu, M. Hagiwara, K. Inazawa, E. Nishimura, Proc. 20th Symp. Dry Process, Inst. Elec. Eng. Tokyo, Japan, 1998, p. 263.
[10] T. Shirafuji, Y. Hayashi, S. Nishino, Mater. Res. Soc. Symp. Proc. Adv. Metall. 1999, 2000, p. 425.
[11] R. d'Agostino, F. Cramarossa, F. Fracassi, F. Illuzzi, in: R. d'Agostino (Ed.), Plasma Deposition Treatment and Etching of Polymers, Academic, New York, 1990, pp. 95–162.
[12] S. Takeishi, H. Kudo, R. Shinohara, M. Hoshino, S. Fukuyama, J. Yamaguchi, M. Yamada, J. Electrochem. Soc. 144 (1997) 1797.